federal register

Friday
October 3, 1980

Part VII

Environmental Protection Agency

Standards of Performance for New Stationary Sources; Addition of Reference Methods 24 and 25 to Appendix A

40 CFR Part 60

[FRL 1525-7]

Standards of Performance for New Stationary Sources; Addition of Reference Methods 24 and 25 to Appendix A

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action establishes two new reference methods to be added to Appendix A of 40 CFR Part 60, Standards of Performance for New Stationary Sources. Reference Method 24 will be used to determine the volatile organic compound (VOC) content of coating materials, and Reference Method 25 will be used to determine the percentage reduction of VOC emissions achieved by emission control devices. These reference methods will be used in several air pollution regulations for industrial surface coatings which are being developed for proposal and promulgation.

EFFECTIVE DATE: October 3, 1980.

ADDRESSES: *Background Information Document.* The Background Information Document (BID) for the promulgated test methods may be obtained from the U.S. EPA Library (MD-35), Research Triangle Park, North Carolina 27711, telephone number (919) 541-2777. Please refer to "Reference Methods 24 and 25—Background Information for Promulgated Test Methods," EPA-450/3-79-030c.

Docket. Docket No. A-79-05, containing all supporting information and public comments, is available for public inspection and copying between 8:00 a.m. and 4:00 pm., Monday through Friday, at EPA's Central Docket Section, Room 2902, Waterside Mall, 401 M Street SW., Washington, D.C. 20460.

FOR FURTHER INFORMATION CONTACT: Mr. Gene W. Smith, Standards Development Branch (MD-13), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541-5421.

SUPPLEMENTARY INFORMATION:

Summary of Reference Methods

Reference Method 24, "Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings," is used to determine the volatile matter content, water content, density, volume solids, and weight fraction solids of paint, varnish, or related surface coatings. Several ASTM standard methods which comprise Method 24 are used to make these determinations. All coatings are analyzed by the same procedure except for the additional step of measuring the water content of waterborne (water reducible) coatings. A data validation procedure is used to establish precision limits for the coating analysis. This verifies the ability of the analyst and the analytical procedure to obtain reproducible results for the coatings tested. In addition for waterborne coatings, the measured parameters are modified by the appropriate confidence limits based on between-laboratory precision statements.

Reference Method 25, "Determination of Total Gaseous Nonmethane Organic Emissions as Carbon," is used to measure the total gaseous nonmethane organics in source emissions. An evacuated cylinder is used to withdraw emission samples from the stack through a chilled condensate trap. After sampling is completed, the contents of the condensate trap and evacuated cylinder are analyzed separately. The organic content of the condensate trap is oxidized to CO_2 which is quantitatively collected in an intermediate collection vessel; a portion of the carbon dioxide is reduced to methane and measured by a flame ionization detector (FID). A portion of the sample collected in the gas sampling tank is injected into a gas chromatograph which separates the nonmethane organics from carbon monoxide, methane, and carbon dioxide; the nonmethane organics are oxidized to carbon dioxide, reduced to methane, and measured by FID. The results of the analyses are combined and reported as total gaseous nonemethane organics.

Background

On October 5, 1979, as an appendix to the proposed standards of performance for automobile and light-duty truck surface coating operations, EPA proposed reference methods for analyzing the volatile organic compound (VOC) content of coatings. These proposed methods were Reference Method 24 (Candidate 1) and (Candidate 2). Candidate 1 expresses the VOC content of surface coating in terms of mass of carbon. Candidate 2, based on the use of several ASTM methods, reports the mass of VOC. Both test methods were proposed to obtain public comment.

Reference Method 25 was proposed at the same time. It measures the volatile organic emissions in effluent streams from stationary sources. When used to measure the inlet and outlet streams of an emission control device, the efficiency of the device can be determined.

These methods would normally be promulgated with the standards of performance for automobile and light-duty truck surface coating operations which are scheduled to be promulgated in the fall of 1980. However, the methods are being promulgated earlier because several changes have been made to the proposed methods, and several regulations are being developed for proposal in the near future which will require the use of these methods. This will allow the public to have the opportunity to comment on the use of these final methods in their respective industries.

Public Participation

During development of the test methods, trade and professional associations and individual companies supplied information and data on these methods. After proposal on October 5, 1979, comments were received from coatings manufacturers and suppliers, trade and professional associations, and State air pollution control agencies. The methods were also discussed at a public hearing held on November 9, 1979. The public comment period was extended from October 5, 1979, to December 14, 1979.

Public Comments and Changes Made to Proposed Reference Methods

Fifteen comment letters were received on the proposed test methods. These comments have been carefully considered and, where determined to be appropriate by the Administrator, changes have been made in the proposed test methods. A detailed discussion of these comments is contained in the background document entitled, "Reference Methods 24 and 25—Background Information for Promulgated Test Methods," which is referred to in the ADDRESSES section of this preamble.

General

The Administrator has rejected proposed Reference Method 24 (Candidate 1) and selected proposed Reference Method 24 (Candidate 2) as the test method to be used to determine the volatile organic content of coatings. Conclusive data were presented by commenters showing that certain coatings representing a significant portion of those in use could not be distilled as required by proposed Method 24 (Candidate 1). For this reason, the Administrator concluded that proposed Method 24 (Candidate 1) is not applicable to all coatings and should not be selected as the reference method.

Several procedural and editorial changes have been made to Reference Method 24 (Candidate 2) and Reference Method 25 as proposed in order to clarify and to improve the sampling and analytical procedures. These changes are based on additional information obtained by EPA from experience with the methods and on the public comments received.

Reference Method 24

The following discussion summarizes the procedural changes made to proposed Reference Method 24, Candidate 2. The procedures were added to protect the source owner from invalid results that might result from poor analytical techniques, application of the method to a coating not suitable for analysis with Reference Method 24, or imprecision in Reference Method 24 resulting from a high percentage of water in the solvent.

The promulgated reference method requires the analyst to complete duplicate analyses on each sample tested. A comparison is then made between these results and the within-laboratory precision statements for each parameter. Duplicate analyses are made until the results fall within the range established for the within-laboratory precision statements. The purpose of the procedures is to verify that the analyst can achieve a level of precision for the coating under analysis equal to or better than the precision obtained by experienced analysts participating in the ASTM studies of the method. Because of the variety of coatings that may be subject to analysis, it is possible that certain coatings may not be amenable to analysis using Reference Method 24; that is, in certain cases it may not be possible to achieve results which meet the precision limits. In this case, the method provides for a case-by-case evaluation and development of a suitable procedure.

An additional procedure for waterborne coatings was added to the promulgated reference method to protect the source owner or operator from a determination of noncompliance when the owner is actually in compliance. This procedure is needed because the results of Reference Method 24 are dependent on the difference between the weight of total solvents and the weight of water. As the percent weight of water increases, the difference decreases. As a result, any imprecision in the measurement of the weight of total solvent in water is magnified in the calculation of organic solvent content. For example, if the total solvent of a coating is measured as 100±2 units and the water content is measured at 90±2 units, the organic solvent content would be in the range of 6 to 14 units. The magnitude of the range, as a percent of the true organic solvent content, increases with increasing water content and could, as shown in the example, lead to a conclusion of noncompliance even when the owner is in compliance. The procedure added to Reference Method 24 for waterborne coatings protects the owner or operator from this erroneous determination by minimizing the calculated value for VOC content. This is done, for example, by subtracting the between-laboratory precision statement from the average value of total solvent and adding the between-laboratory precision statement to the average value for water content. Thus, if a source owner is in compliance based on average coating values, the compliance method will automatically show a lower VOC content because of the adjustments made to the average values based on the between-laboratory precision statements.

Based on comments from manufacturers that ASTM 2697 has only been shown to be applicable to architectural coatings, the analytical procedure for determining volume solids has been eliminated from Reference Method 24. The commenters stated that this ASTM procedure was not applicable to all the coatings that Method 24 was intended to cover. Therefore, Method 24 requires that the volume solids be calculated from manufacturer's formulation data.

The coatings classifications step in the proposed method was eliminated because industry comments indicated that it was only necessary to separate waterborne (water reducible) and solvent-borne (solvent reducible) coatings. Therefore, the "Procedure" discussed in Section 4 of the proposed method has been simplified.

Several commenters recommended that the use of coatings manufacturers' data be allowed in calculating VOC content of coatings rather than required Method 24. Coatings manufacturers' data will be allowed in calculating VOC content of coatings because this will reduce the burden on the industry to measure all coatings with Method 24. Use of this method to calculate VOC content of coatings will require industries to closely monitor and record all organic solvents added to the coatings at the plant. Method 24 will be the reference method.

One commenter suggested that EPA should specify the volume fraction of solids for the various types of coatings similar to the way transfer efficiencies were listed. Based on comments from manufacturers that ASTM 2697 has only been shown to be applicable to architectural coatings, the volume fraction of solids determination in Method 24 has been removed. Method 24 specifies the use of manufacturer's formulation data for calculating volume fraction of solids.

Reference Method 25

The majority of the procedural changes made to Method 25 relate to calibration requirements and are meant to improve quality assurance and at the same time simplify the daily operation of the analytical equipment. This is accomplished by requiring performance tests on the analytical equipment (nonmethane organic analyzer and condensate recovery and conditioning apparatus) prior to initial use; specific criteria for the performance tests are provided. Routine daily calibrations (much less time consuming than previously required) are conducted and the results are compared to performance test reference values to determine whether the performance of the analytical equipment is still acceptable.

In the promulgated test method, several important system components are not specified; instead, minimum performance specifications for these components are provided. The method is written in this manner to allow individual preference in choosing components, as well as to encourage development and use of improved components. Therefore, Addendum I which lists specific information regarding system components found to be acceptable has been added to the method to provide guidance for users.

Specifics of the most important procedural changes that have been included in the promulgated test method are as follows:

1. Section 1.1. Applicability. This section was rewritten to clarify the applicability of Method 25 in relation to several other organic measurement methods.

2. Section 2.2.2 Nonmethane Organic Analyzer. The reference to the analyzer is changed from "total gaseous nonmethane organic analyzer" to nonmethane organic analyzer (NMO). The description is clarified to indicate that the NMO analyzer is also used to quantify CO_2 from trap condensate recovery. Furthermore, a requirement that the NMO analyzer meet an initial performance test with specific criteria is added. Previously, only demonstration of "proper separation, oxidation, reduction and measurement" was required.

3. Section 4.1.3 Pretest Leak Check. The leak check procedure is simplified. Instead of evacuating the sample train,

the sample probe is plugged and then the sample value is opened; the sample tank vacuum gauge is monitored for a change in vacuum.

4. Section 4.1.4 Sample Train Operation. This section is clarified to indicate that any probe extension used must be positioned totally in the stack effluent; any portion of the sample probe outside the stack wall must be analyzed as part of the condensate trap.

5. Section 4.1.5 Post Test Leak Check. The leak check procedure is simplified (see "3" above).

6. Section 4.3.3 Recovery of Condensate Trap Sample. A requirement for mixing auxiliary oxygen with the carrier gas just prior to the catalyst is added. The procedures are clarified to indicate that the condensate trap is placed in a muffle furnace at 500°C (changed from 600°C) and that the probe must be heated.

7. Section 5.1 Initial Performance Check for Condensate Recovery and Conditioning Apparatus. A requirement is added for an initial performance test of the system which includes a carrier gas blank value determination (section 5.1.1), and oxidation catalyst efficiency check (section 5.1.2), and an overall system performance check via liquid injections (section 5.1.3). Previously, only a catalyst efficiency check was required.

8. Section 5.2 Initial NMO Analyzer Performance Test. The calibration criteria for the NMO analyzer are changed to include an initial performance test. This performance test requires an oxidation catalyst check (5.2.1), and an analyzer linearity check (5.2.2), determination of a NMO calibration response factor (5.2.2), determination of a CO_2 calibration response factor (5.2.3), determination of a NMO blank value (5.2.4) and a system check using several gaseous organic compounds (5.2.5).

9. Section 5.3 NMO Daily Calibration. This section requires that a daily calibration of the NMO analyzer be conducted. The calibration involves one CO_2 calibration gas and one propane calibration gas. Response factors are determined for both CO_2 and NMO, and a NMO blank value is measured. This calibration is conducted with the oxidation and reduction catalysts in full operation. The results obtained are compared to the reference values obtained during the initial performance test in order to determine if the analyzer performance is acceptable. This daily calibration procedure is greatly simplified compared to the procedure previously required which included bypassing the oxidation and reduction catalysts and using several different concentration levels of methane, carbon dioxide and propane calibration gases.

10. Section 6.2 Noncondensible Organics. The calculation for the NMO concentration of the contents of each collection tank is changed by rewriting the equation to include the subtraction of the daily NMO blank value from the measured concentration.

11. Section 6.3 Condensible Organics. The calculation for the NMO concentration of the contents of each condensate trap is changed by rewriting the equation to include the substraction of the daily condensate recovery and conditioning system carrier blank value from the measured CO_2 concentration.

Other Comments

1. One commenter noted that the drying time was different for ASTM D–2369 and ASTM D–2697, and that these procedures were not consistent with each other. Since ASTM D–2697 has been deleted, this comment is no longer applicable.

2. Three commenters recommended that the direct use of a flame ionization detection (FID) system or similar instrumentation systems be allowed instead of Method 25. The specific comments made and EPA's responses are as follows:

a. *Direct FID is simpler and more precise.* While the direct use of an FID system is simpler than Method 25, it will not give accurate results in many situations because the instrument response varies with different compounds. Therefore, the FID system cannot be considered an adequate reference method, but may be acceptable as an alternative compliance procedure on a case-by-case basis as allowed in 40 CFR 60.8(b).

b. *The ability to conduct on-site analyses and DOT restrictions associated with shipping organic samples from a source location to a laboratory make the FID preferable.* The ability to use the FID system to conduct on-site analyses is not in itself sufficient justification to allow the use of direct flame ionization detection. DOT regulations regarding shipment of hazardous materials do require that great care be taken in shipping the test samples. The DOT regulations impose strict packaging requirements on flammable liquids and compressed flammable gases. However, exemptions for the strict packaging requirements are permitted for most liquids if less than one quart is shipped (see 49 CFR 172.101). In addition, the gas sample tanks likely to be shipped from an on-site location to a laboratory for analyses do not meet the DOT definition of a compressed flammable gas because the sample tanks are not under high pressure and, therefore, should not pose a shipping problem (see 49 CFR 173.300).

Miscellaneous

This final rulemaking is issued under the authority of Sections 111, 114, and 301(a) of the Clean Air Act as amended (42 U.S.C. 7411, 7414, and 7601(a)).

Dated: September 25, 1980.

Douglas M. Costle,

Administrator.

Appendix A of 40 CFR Part 60 is amended by adding Reference Methods 24 and 25 as follows:

Appendix A—Reference Methods

* * * * *

Method 24—Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D 1475–60. Standard Method of Test for Density of Paint, Lacquer, and Related Products.

2.2 ASTM D 2369–81. Provisional Method of Test for Volatile Content of Paints.

2.3 ASTM D 3792–79. Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph.

2.4 ASTM Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method.

3. Procedure

3.1 Volatile Matter Content. Use the procedure in ASTM D 2369–81 to determine the volatile matter content (may include water) of the coating. Record the following information:

W_1 = Weight of dish and sample before heating, g.

W_2 = Weight of dish and sample after heating, g.

W_3 = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_3} \quad \text{Eq. 24-1}$$

Record the arithmetic average (W_v).

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W_w) using either "Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph" or "Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method." A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in section 4.3 is met. Record the arithmetic average (W_w).

3.3 Coating Density. Determine the density (D_c, kg/liter) of the surface coating using the procedure in ASTM D 1475–60.

Run duplicate sets of determinations for each coating until the criterion in section 4.3 is met. Record the arithmetic average (D_c).

3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, W_v	1.5 pct W_v	4.7 pct W_v.
Water content, W_w	2.9 pct W_w	7.5 pct W_w.
Density, D_c	0.001 kg/liter	0.002 kg/liter.

4.3 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD–13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropirate between-laboratory precision value to the measured mean value for that parameter. For W_v and D_c use the lower confidence limits, and for W_w, use the upper confidence limit. Because V_s is calculated, there is no adjustment for the parameter.

5. Calculations

5.1 Nonaqueous Volatile Matter.

5.1.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24–2}$$

Where:

W_o = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24–3}$$

5.2 Weight fraction solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24–4}$$

Where: W_s = Weight solids, g/g.

6. Bibliography

6.1 Provisional Method Test for Volatile Content of Paints. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 2369–81.

6.2 Standard Method of Test for Density of Paint, Varnish, Lacquer, and Related Products. In: 1980 Book of ASTM Standards, Part 27. Philadelphia, Pennsylvania, ASTM Designation D 1475–60. 1980.

6.3 Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 3792–79.

6.4 Provisional Method of Test Water in Paint or Related Coatings by the Karl Fischer Titration Method. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and therefore, in some cases, an in-stack particulate filter is required. This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semi-continuous nonmethane organic (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semi-continuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane will, of course, also be measured. In practice, the FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and *only* the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide (CO_2) which is quantitatively collected in an evacuated vessel; then a portion of the CO_2 is reduced to methane (CH_4) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide (CO), CO_2 and CH_4; the nonmethane organics (NMO) are oxidized to

CO_2, reduced to CH_4, and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

2. Apparatus

The sampling system consists of a condensate trap, flow control system, and sample tank (Figure 1). The analytical system consists of two major sub-systems: an oxidation system for the recovery and conditioning of the condensate trap contents and a NMO analyzer. The NMO analyzer is a GC with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. (Figures 2 and 3 are schematics of a typical NMO analyzer.) The system for the recovery and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (Figure 4 is a schematic of a typical system.) TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. NMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory.

2.1 Sampling. The following equipment is required:

2.1.1 Probe. 3.2-mm OD (⅛-in.) stainless steel tubing.

2.1.2 Condensate Trap. Constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 5.

2.1.3 Flow Shut-off Valve. Stainless steel control valve for starting and stopping sample flow.

2.1.4 Flow Control System. Any system capable of maintaining the sampling rate to within ±10 percent of the selected flow rate (50 to 100 cc/min range).

2.1.5 Vacuum Gauge. Gauge for monitoring the vacuum of the sample tank during leak checks and sampling.

2.1.6 Sample Tank. Stainless steel or aluminum tank with a volume of 4 to 8 liters, equipped with a stainless steel female quick connect for assembly to the sample train and analytical system.

2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.1.8 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2 Analysis. The following equipment is required:

2.2.1 Condensate Recovery and Conditioning Apparatus. An apparatus for recovering and catalytically oxidizing the condensate trap contents is required. Figure 4 is a schematic of such a system. The analyst must demonstrate prior to initial use that the analytical system is capable of proper oxidation and recovery, as specified in section 5.1. The condensate recovery and conditioning apparatus consists of the following major components.

2.2.1.1 Heat Source. A heat source sufficient to heat the condensate trap (including probe) to a temperature where the trap turns a "dull red" color. A system using both a propane torch and an electric muffle-type furnace is recommended.

2.2.1.2 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.1.2). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.1.3 Water Trap. Any leak-proof moisture trap capable of removing moisture from the gas stream.

2.2.1.4 NDIR Detector. A detector capable of indicating CO_2 concentration in the zero to 1 percent range. This detector is required for monitoring the progress of combustion of the organic compounds from the condensate trap.

2.2.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the trap conditioning system at a near constant pressure.

2.2.1.6 Intermediate Collection Vessel. Stainless steel or aluminum collection vessel equipped with a female quick connect. Tanks with nominal volumes in the 1 to 4 liter range are recommended.

2.2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.2.1.8 Gas Purifiers. Gas purification systems sufficient to maintain CO_2 and organic impurities in the carrier gas and auxiliary oxygen at a level of less than 10 ppm (may not be required depending on quality of cylinder gases used).

2.2.2 NMO Analyzer. Semi-continuous GC/FID analyzer capable of: (1) separating CO, CO_2, and CH_4 from nonmethane organic compounds, (2) reducing the CO_2 to CH_4 and quantifying as CH_4 and (3) oxidizing the nonmethane organic compounds to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4. The analyst must demonstrate prior to initial use that the analyzer is capable of proper separation, oxidation, reduction, and measurement (section 5.2). The analyzer consists of the following major components:

2.2.2.1 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.1). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.2 Reduction Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.3). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.3 Separation Column(s). Gas chromatographic column(s) capable of separating CO, CO_2, and CH_4 from NMO compounds as demonstrated according to the procedures established in this method (section 5.2.5). Addendum I of this method lists a column found to be acceptable.

2.2.2.4 Sample Injection System. A GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1 cc loop recommended).

2.2.2.5 FID. A FID meeting the following specifications is required.

2.2.2.5.1 Linearity. A linear response (± 5%) over the operating range as demonstrated by the procedures established in section 5.2.2.

2.2.2.5.2 Range. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale for a full scale range of 10 to 50000 ppm CH_4.

2.2.2.6 Data Recording System. Analog strip chart recorder or digital intergration system compatible with the FID for permanently recording the analytical results.

2.2.3 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

2.2.4 Thermometer. Capable of measuring the laboratory temperature within 1°C.

2.2.5 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2.6 Syringe (2). 10 μl and 100 μl liquid injection syringes.

2.2.7 Liquid Sample Injection Unit. 316 SS U-tube fitted with a Teflon injection septum, see Figure 6.

3. Reagents

3.1 Sampling. Crushed dry ice is required during sampling.

3.2 Analysis.

3.2.1 NMO Analyzer. The following gases are needed:

3.2.1.1 Carrier Gas. Zero grade gas containing less than 1 ppm C. Addendum I of this method lists a carrier gas found to be acceptable.

3.2.1.2 Fuel Gas. Pure hydrogen, containing less than 1 ppm C.

3.2.1.3 Combustion Gas. Zero grade air or oxygen as required by the detector.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. Five percent O_2 in N_2, containing less than 1 ppm C.

3.2.2.2 Auxiliary Oxygen. Zero grade oxygen containing less than 1 ppm C.

3.2.2.3 Hexane. ACS grade, for liquid injection.

3.2.2.4 Toluene. ACS grade, for liquid injection.

3.3 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ± 5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required.

3.3.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

3.3.2 Flame Ionization Detector Linearity and Nonmethane Organic Calibration Gases (3). Gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

3.3.3 Carbon Dioxide Calibration Gases (3). Gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air. Note: total NMO less than 1 ppm required for 1 percent mixture.

3.3.4 NMO Analyzer System Check Calibration Gases (4).

3.3.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 20 ppm C_3H_8, prepared in air.

3.3.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

3.3.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

3.3.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

4. Procedure

4.1 Sampling.

4.1.1 Sample Tank Evacuation and Leak Check. Either in the laboratory or in the field, evacuate the sample tank to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer) then leak check the sample tank by isolating the tank from the vacuum pump and allowing the tank to sit for 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

4.1.2 Sample Train Assembly. Just prior to assembly, measure the tank vaccuum using a mercury U-tube manometer. Record this vaccum (P_{ti}), the ambient temperature (T_{ti}), and the barometric pressure (P_{bi}) at this time. Assuring that the flow shut-off valve is in the closed position, assemble the sampling system as shown in Figure 1. Immerse the condensate trap body in dry ice to within 2.5 or 5 cm of the point where the inlet tube joins the trap body.

4.1.3. Pretest Leak Check. A pretest leak check is required. After the sampling train is assembled, record the tank vacuum as indicated by the vaccum gauge. Wait a minimum period of 10 minutes and recheck the indicated vacuum. If the vacuum has not changed, the portion of the sampling train behind the shut-off valve does not leak and is considered acceptable. To check the front portion of the sampling train, assure that the probe tip is tightly plugged and then open the sample train flow shut-off valve. Allow the sample train to sit for a minimum period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the pretest leak rate (cm/Hg per 10 minutes). At the completion of the leak check period, close the sample flow shut-off valve.

4.1.4. Sample Train Operation. Place the probe into the stack such that the probe is perpendicular to the direction of stack gas flow; locate the probe tip at a single preselected point. If a probe extension which will not be analyzed as part of the condensate trap is being used, assure that at least a 15 cm section of the probe which will be analyzed with the trap is in the stack effluent. For stacks having a negative static pressure, assure that the sample port is sufficiently sealed to prevent air in-leakage around the probe. Check the dry ice level and add ice if necessary. Record the clock time and sample tank gauge vacuum. To begin sampling, open the flow shut-off valve and adjust (if applicable) the control valve of the flow control system used in the sample train; maintain a constant flow rate (±10 percent) throughout the duration of the sampling period. Record the gauge vacuum and flowmeter setting (if applicable) at 5-minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulation; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained due to reduced sample tank vacuum. When the sampling is completed, close the flow shut-off valve and record the final sample time and guage vacuum readings. Note: If the sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After removing the probe from the stack, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train) and connect another sample tank to the sampling train. Prior to attaching the new tank to the sampling train, assure that the tank vacuum (measured on-site by the U-tube manometer) has been recorded on the data form and that the tank has been leak-checked (on-site). After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

4.1.5 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, remove the probe from the stack and plug the probe tip. Open the sample train flow shut-off valve and monitor the sample tank vacuum gauge for a period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the post test leak rate (cm Hg per 10 minutes). If the sampling train does not pass the post leak check, invalidate the run or use a procedure acceptable to the Administrator to adjust the data.

4.2 Sample Recovery. After the post test leak check is completed, disconnect the condensate trap at the flow metering system and tightly seal both ends of the condensate trap. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Remove the flow metering system from the sample tank. Attach the U-tube manometer to the tank (keep length of connecting line to a minimum) and record the final tank vacuum (P_t); record the tank temperature (T_t) and barometric pressure at this time. Disconnect the manometer from the tank. Assure that the test run number is properly identified on the condensate trap and the sample tank(s).

4.3 Condensate Recovery and Conditioning. Prepare the condensate recovery and conditioning apparatus by setting the carrier gas flow rate and heating the catalyst to its operating temperature. Prior to initial use of the condensate recovery and conditioning apparatus, a system performance test must be conducted according to the procedures established in section 5.1 of this method. After successful completion of the initial performance test, the system is routinely used for sample conditioning according to the following procedures:

4.3.1 System Blank and Catalyst Efficiency Check. Prior to and immediately following the conditioning of each set of sample traps, or on a daily basis (whichever occurs first) conduct the carrier gas blank test and catalyst efficiency test as specified in sections 5.1.1 and 5.1.2 of this method. Record the carrier gas initial and final blank values, B_{ti} and B_{tf}, respectively. If the criteria of the tests cannot be met, make the necessary repairs to the system before proceeding.

4.3.2 Condensate Trap Carbon Dioxide Purge and Sample Tank Pressurization. The first step in analysis is to purge the condensate trap of any CO_2 which it may contain and to simultaneously pressurize the sample tank. This is accomplished as follows: Obtain both the sample tank and condensate trap from the test run to be analyzed. Set up the condensate recovery and conditioning apparatus so that the carrier flow bypasses the condensate trap hook-up terminals, bypasses the oxidation catalyst, and is vented to the atmosphere. Next, attach the condensate trap to the apparatus and pack the trap in dry ice. Assure that the valves isolating the collection vessel connection from the atmospheric vent and the vacuum pump are closed and then attach the sample tank to the system as if it were the intermediate collection vessel. Record the tank vacuum on the laboratory data form. Assure that the NDIR analyzer indicates a zero output level and then switch the carrier flow through the condensate trap; immediately switch the carrier flow from vent to collect. The condensate trap recovery and conditioning apparatus should now be set up as indicated in Figure 8. Monitor the NDIR; when CO_2 is no longer being passed through the system, switch the carrier flow so that it once again bypasses the condensate trap. Continue in this manner until the gas sample tank is pressurized to a nominal gauge pressure of 800 mm Hg. At this time, isolate the tank, vent the carrier flow, and record the sample tank pressure (P_{tf}), barometric pressure (P_{bf}), and ambient temperature (T_{tf}). Remove the sample tank from the system.

4.3.3 Recovery of Condensate Trap Sample. Oxidation and collection of the sample in the condensate trap is now ready to begin. From the step just completed in section 4.3.1.2 above, the system should be set up so that the carrier flow bypasses the condensate trap, bypasses the oxidation catalyst, and is vented to the atmosphere. Attach an evacuated intermediate collection vessel to the system and then switch the carrier so that it flows through the oxidation catalyst. Switch the carrier from vent to collect and open the valve to the collection vessel; remove the dry ice from the trap and then switch the carrier flow through the trap. The system should now be set up to operate as indicated in Figure 9. During oxidation of the condensate trap sample, monitor the NDIR to determine when all the sample has been removed and oxidized (indicated by return to baseline of NDIR analyzer output). Begin heating the condensate trap and probe with a propane torch. The trap should be heated to a temperature at which the trap glows a "dull red" (approximately 500°C). During the early part of the trap "burn out," adjust the carrier and auxiliary oxygen flow rates so that an excess of oxygen is being fed to the catalyst system. Gradually increase the flow of carrier gas through the trap. After the NDIR indicates that most of the organic matter has been purged, place the trap in a muffle furnance (500°C). Continue to heat the probe with a torch or some other procedure (e.g., electrical resistance heater). Continue this procedure for at least 5 minutes after the NDIR has returned to baseline. Remove the heat from the trap but continue the carrier flow until the intermediate collection vessel is pressurized to a gauge pressure of 800 mm

Hg (nominal). When the vessel is pressurized, vent the carrier; measure and record the final intermediate collection vessel pressure (P_f) as well as the barometric pressure (P_{bv}), ambient temperature (T_v), and collection vessel volume (V_v).

4.4 Analysis. Prior to putting the NMO analyzer into routine operation, an initial performance test must be conducted. Start the analyzer and perform all the necessary functions in order to put the analyzer in proper working order, then conduct the performance test according to the procedures established in section 5.2. Once the performance test has been successfully completed and the CO_2 and NMO calibration response factors determined, proceed with sample analysis as follows:

4.4.1 Daily operations and calibration checks. Prior to and immediately following the analysis of each set of samples or on a daily basis (whichever occurs first) conduct a calibration test according to the procedures established in section 5.3. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (section 5.2) before proceeding.

4.4.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample and then inject a preliminary sample in order to determine the appropriate FID attenuation. Inject triplicate samples from the intermediate collection vessel and record the values obtained for the condensible organics as CO_2 (C_{cm}).

4.4.3 Analysis of Sample Tank. Purge the sample loop with sample and inject a preliminary sample in order to determine the appropriate FID attenuation for monitoring the backflushed non-methane organics. Inject triplicate samples from the sample tank and record the values obtained for the nonmethane organics (C_{tm}).

5. Calibration and Operational Checks

Maintain a record of performance of each item.

5.1 Initial Performance Check of Condensate Recovery and Conditioning Apparatus.

5.1.1 Carrier Gas and Auxiliary Oxygen Blank. Set equal flow rates for both the carrier gas and auxiliary oxygen. With the trap switching valves in the bypass position and the catalyst in-line, fill an evacuated intermediate collection vessel with carrier gas. Analyze the collection vessel for CO_2; the carrier blank is acceptable if the CO_2 concentration is less than 10 ppm.

5.1.2 Catalyst Efficiency Check. Set up the condensate trap recovery system so that the carrier flow bypasses the trap inlet and is vented to the atmosphere at the system outlet. Assure that the valves isolating the collection system from the atmospheric vent and vacuum pump are closed and then attach an evacuated intermediate collection vessel to the system. Connect the methane standard gas cyclinder (section 3.3.1) to the system's condensate trap connector (probe end, Figure 4). Adjust the system valving so that the standard gas cylinder acts as the carrier gas and adjust the flow rate to the rate normally used during trap sample recovery. Switch off the auxiliary oxygen flow and then switch from vent to collect in order to begin collecting a sample. Continue collecting a sample in a normal manner until the intermediate vessel is filled to a nominal gauge pressure of 300 mm Hg. Remove the intermediate vessel from the system and vent the carrier flow to the atmosphere. Switch the valving to return the system to its normal carrier gas and normal operating conditions. Analyze the collection vessel for CO_2; the catalyst efficiency is acceptable if the CO_2 concentration is within ±5 percent of the expected value.

5.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 6. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap and set the carrier gas and auxiliary oxygen flow rates to normal operating levels. Attach an evacuated intermediate collection vessel to the system and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see. 5.1.3.1 to 5.1.3.4) via the injection septum. Heat the injection unit with a torch while monitoring the oxidation reaction on the NDIR. Continue the purge until the reaction is complete. Measure the final collection vessel pressure and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery using the equation in section 6.6.

The performance test is acceptable if the average percent recovery is 100 ± 10 percent with a relative standard deviation (section 6.7) of less than 5 percent for each set of triplicate injections as follows:

5.1.3.1 100 μl hexane.
5.1.3.2 10 μl hexane.
5.1.3.3 100 μl toluene.
5.1.3.4 10 μl toluene.

5.2 Initial NMO Analyzer Performance Test.

5.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (section 3.3.1). The oxidation catalyst operation is acceptable if no FID response is noted.

5.2.2 Analyzer Linearity Check and NMO Calibration. Operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 3.3. make triplicate injections of each calibration gas and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within ±5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ±5 percent. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}).

5.2.3 Reduction Catalyst Efficiency Check and CO_2 Calibration. An exact determination of the reduction catalyst efficiency is not required. Instead, proper catalyst operation is indirectly checked and continuously monitored by establishing a CO_2 response factor and comparing it to the NMO response factor. Operating both the oxidation and reduction catalysts make triplicate injections of each of the CO_2 calibration gases (section 3.3.3). Calculate the average response factor (area/ppm) for each calibration gas, as well as the overall mean of the response factor values. The reduction catalyst operation is acceptable if the average response factor of each calibration gas is within ±5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ±5 percent. Additionally, the CO_2 overall mean response factor must be within ±10 percent of the NMO calibration response factor (RF_{NMO}) calculated in section 5.2.2. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}).

5.2.4 NMO System Blank. For the high level CO_2 calibration gas (section 3.3.3) record the NMO value measured during the CO_2 calibration conducted in section 5.2.3. This value is the NMO blank value for the analyzer (B_a) and should be less than 10 ppm.

5.2.5 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 3.3.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within ±12 percent of the expected value.

5.3 NMO Analyzer Daily Calibration.

5.3.1 NMO Blank and CO_2. Inject triplicate samples of the high level CO_2 calibration gas (section 3.3.3) and calculate the average response factor. The system operation is adequate if the calculated response factor is within ±10 percent of the RF_{CO2} calculated during the initial performance test (section 5.2.2). Use the daily response factor (DRF_{co2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the collection vessel samples. In addition, record the NMO blank value (B_a); this value should be less than 10 ppm.

5.3.2 NMO Calibration. Inject triplicate samples of the mixed propane calibration cylinder (section 3.3.4.1) and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within ±10 percent of the RF_{NMO} calculated during the initial performance test (section 5.2.1). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

5.4 Sample Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in service, determine the tank volume by weighing the tanks empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

5.5 Intermediate Collection Vessel. The volume of the intermediate collection vessels used to collect CO_2 during the analysis of the condensate traps must be determined. Prior to putting each vessel into service, determine the volume by weighing the vessel empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

BILLING CODE 6560-01-M

6. Calculations

Note: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge pressure.

6.1 Sample Volume. For each test run, calculate the gas volume sampled:

$$V_s = 0.386\ V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right)$$

6.2 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C):

$$C_t = \left[\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right] \left[\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} - B_a \right]$$

6.3 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C):

$$C_c = 0.386 \frac{V_v P_f}{V_s T_f} \left[\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} - B_t \right]$$

6.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_t + C_c$$

6.5 Total Gaseous Nonmethane Organics (TGNMO) Mass Concentration. To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

$$M_c = 0.498\ C$$

6.6 Percent Recovery. To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system use the following equation:

$$\text{percent recovery} = 1.6 \frac{M}{L} \frac{V_v}{\rho} \frac{P_f}{T_f} \frac{C_{cm}}{N}$$

6.7 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{X}} \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n - 1}}$$

BILLING CODE 6560-01-C

Where:

B_a = Measured NMO blank value for NMO analyzer, ppm C.

B_t = Measured CO_2 blank value for condensate recovery and conditioning system carrier gas, ppm CO_2.

C = total gaseous nonmethane organic (TGNMO) concentration of the effluent, ppm C equivalent.

C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.

C_{cm} = Measured concentration (NMO analyzer) for the condensate trap (intermediate collection vessel), ppm CO_2.

C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.

C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.

L = Volume of liquid injected, microliters.

M = Molecular weight of the liquid injected, g/g-mole.

M_c = total gaseous non-methane organic (TGNMO) mass concentration of the effluent, mg C/dscm.

N = Carbon number of the liquid compound injected (N=7 for toluene, N=6 for hexane).

P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.

P_{ti} = Gas sample tank pressure prior to sampling, mm Hg absolute.

P_t = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg absolute.

P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.

T_f = Final temperature of intermediate collection vessel, °K.

T_{ti} = Sample tank temperature prior to sampling, °K.

T_t = Sample tank temperature at completion of sampling, °K.

T_{tf} = Sample tank temperature after pressurizing °K.

V = Sample tank volume, cm.

V_v = Intermediate collection vessel volume, cm.

V_s = Gas volume sampled, dscm.

n = Number of data points.

q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 . . . q).

r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).

x_i = Individual measurements.

X = Mean value.

p = Density of liquid injected, g/cc.

7. Bibliography

7.1 Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2 (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

7.2 Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

Method 25

Addendum I. System Components

In test Method 25 several important system components are not specified; instead minimum performance specifications are provided. The method is written in this manner to permit individual preference in choosing components, as well as to encourage development and use of improved components. This addendum is added to the method in order to provide users with some specific information regarding components which have been found satisfactory for use with the method. This listing is given only for the purpose of providing information and does not constitute an endorsement of any product by the Environmental Protection Agency. This list is not meant to imply that other components not listed are not acceptable.

1. Condensate Recovery and Conditioning System Oxidation Catalyst. ⅜" OD×14" inconel tubing packed with 8 inches of hopcalite* oxidizing catalyst and operated at 800°C in a tube furnace. Note: At this temperature, this catalyst must be purged with carrier gas at all times to prevent catalyst damage.

2. NMO Analyzer Oxidation Catalyst. ¼" OD×14" inconel tubing packed with 6 inches of hopcalite oxidizing catalyst and operated at 800°C in a tube furnace. (See note above.)

3. NMO Analyzer Reduction Catalyst. Reduction Catalyst Module; Byron Instruments, Raleigh, N.C.

4. Gas Chromatographic Separation Column. ⅛ inch OD stainless steel packed with 3 feet of 10 percent methyl silicone, Sp 2100 (or equivalent) on Supelcoport (or equivalent), 80/100 mesh, followed by 1.5 feet Porapak Q (or equivalent) 60/80 mesh. The inlet side is to the silicone. Condition the column for 24 hours at 200°C with 20 cc/min N_2 purge.

During analysis for the nonmethane organics the separation column is operated as follows: First, operate the column at −78°C (dry ice bath) to elute CO and CH_4. After the CH_4 peak operate the column at 0°C to elute CO_2. When the CO_2 is completely eluted, switch the carrier flow to backflush the column and simultaneously raise the column temperature to 100°C in order to elute all nonmethane organics (exact timings for column operation are determined from the calibration standard).

Note.—The dry ice operating condition may be deleted if separation of CO and CH_4 is unimportant.

Note.—Ethane and ethylene may or may not be measured using this column; whether or not ethane and ethylene are quantified will depend on the CO_2 concentration in the gas sample. When high levels of CO_2 are present, ethane and ethylene will elute under the tail of the CO_2 peak.

5. Carrier Gas. Zero grade nitrogen or helium or zero air.

BILLING CODE 6560-01-M

*MSA registered trademark.

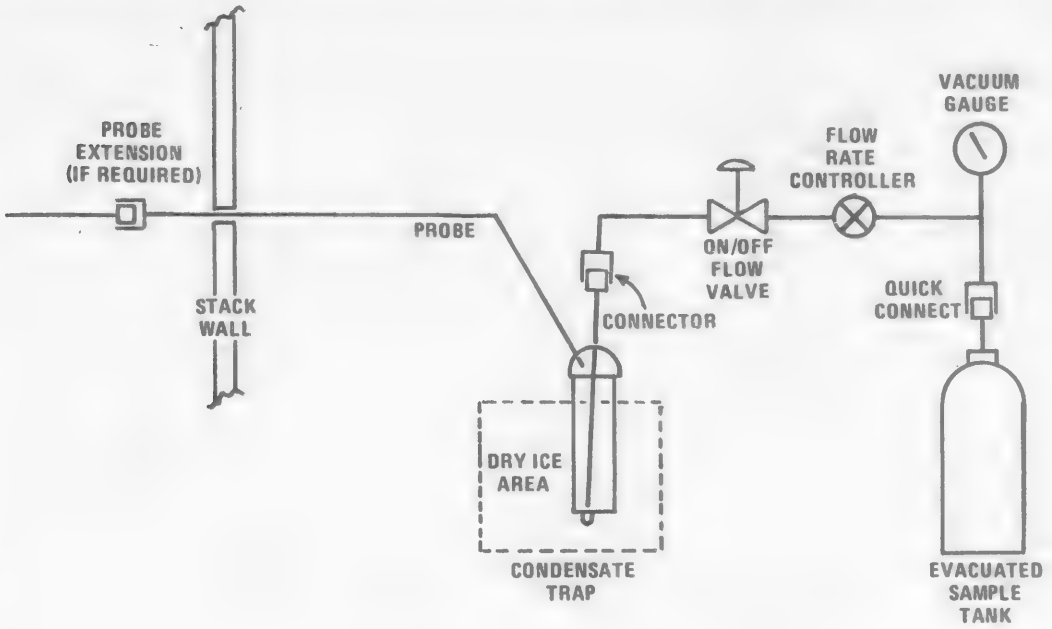

Figure 1. Sampling apparatus.

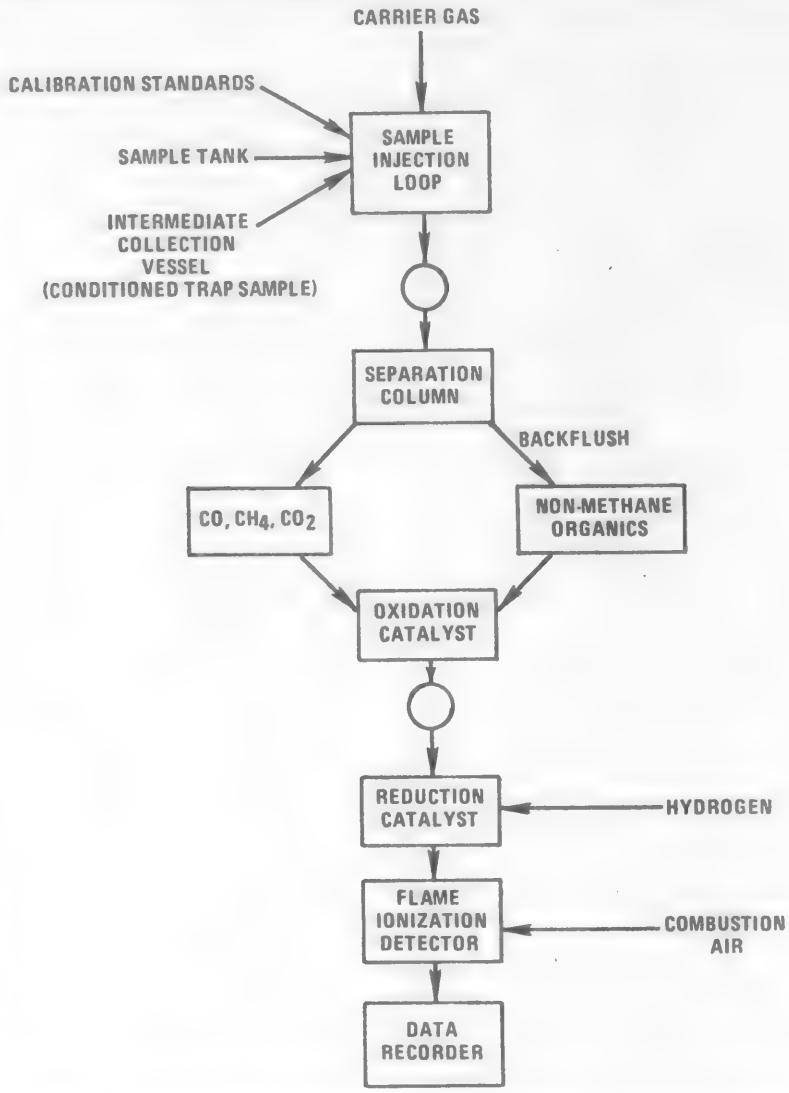

Figure 2. Simplified schematic of non-methane organic (NMO) analyzer.

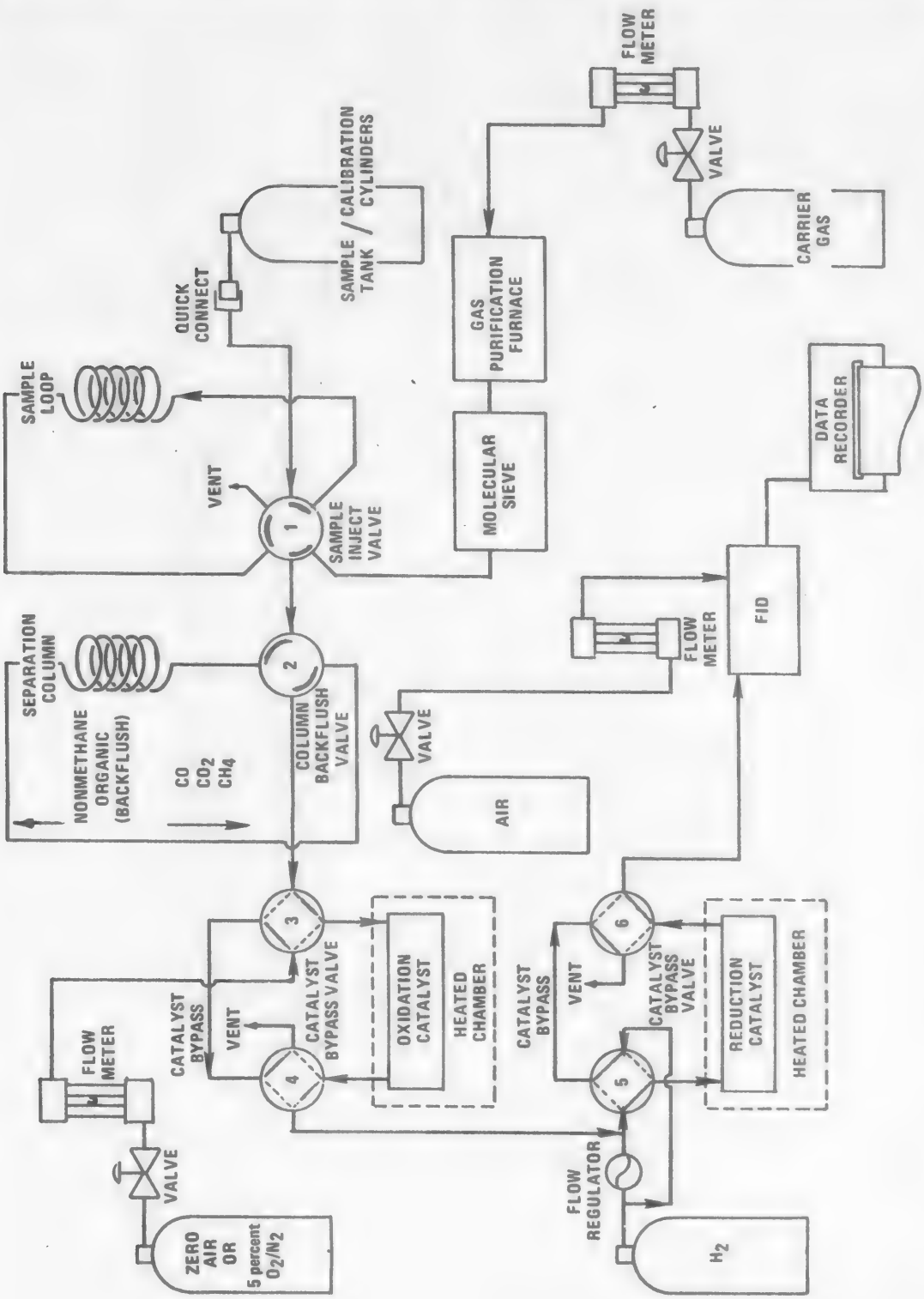

Figure 3. Nonmethane organic (NMO) analyzer.

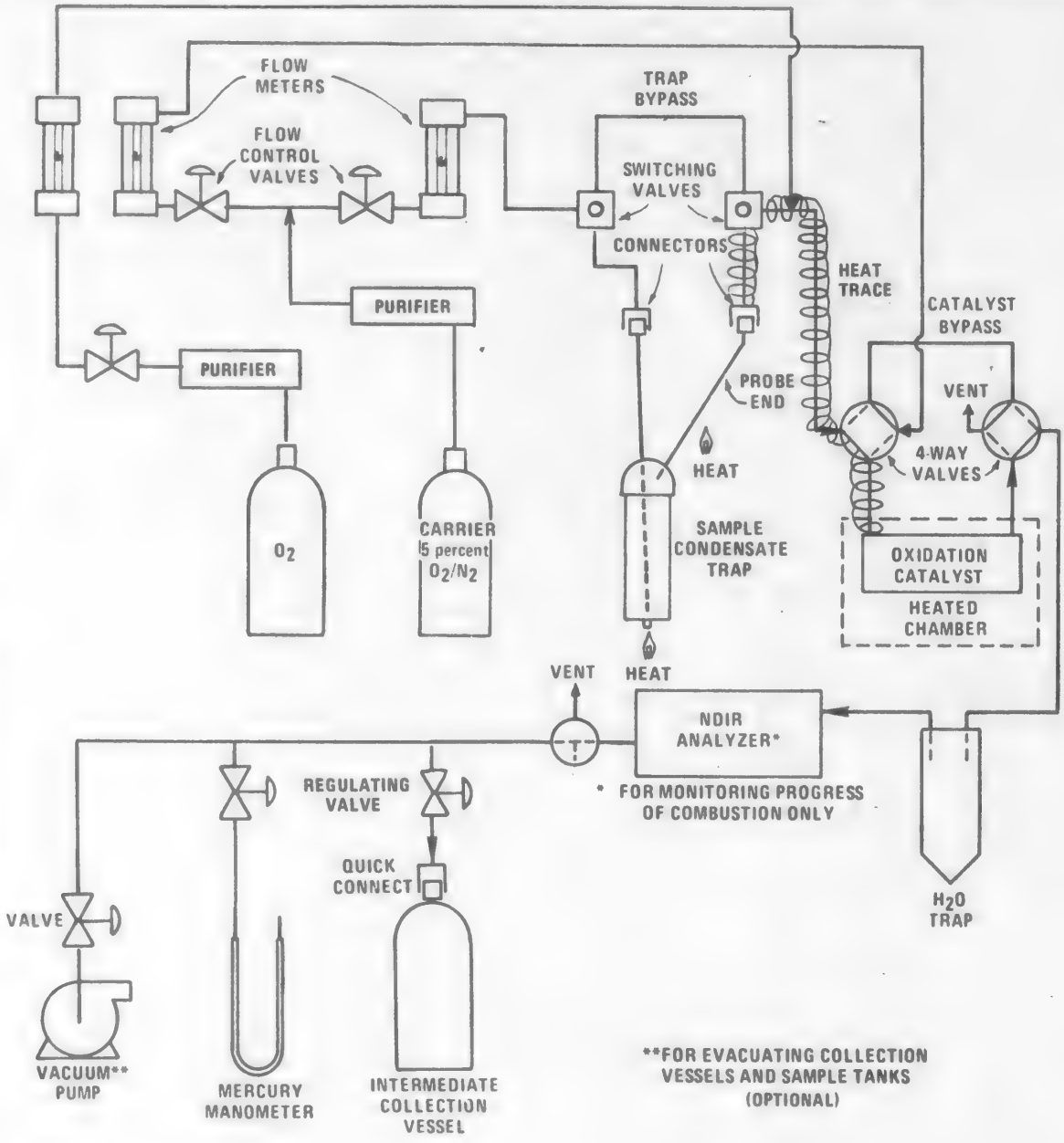

Figure 4. Condensate recovery and conditioning apparatus.

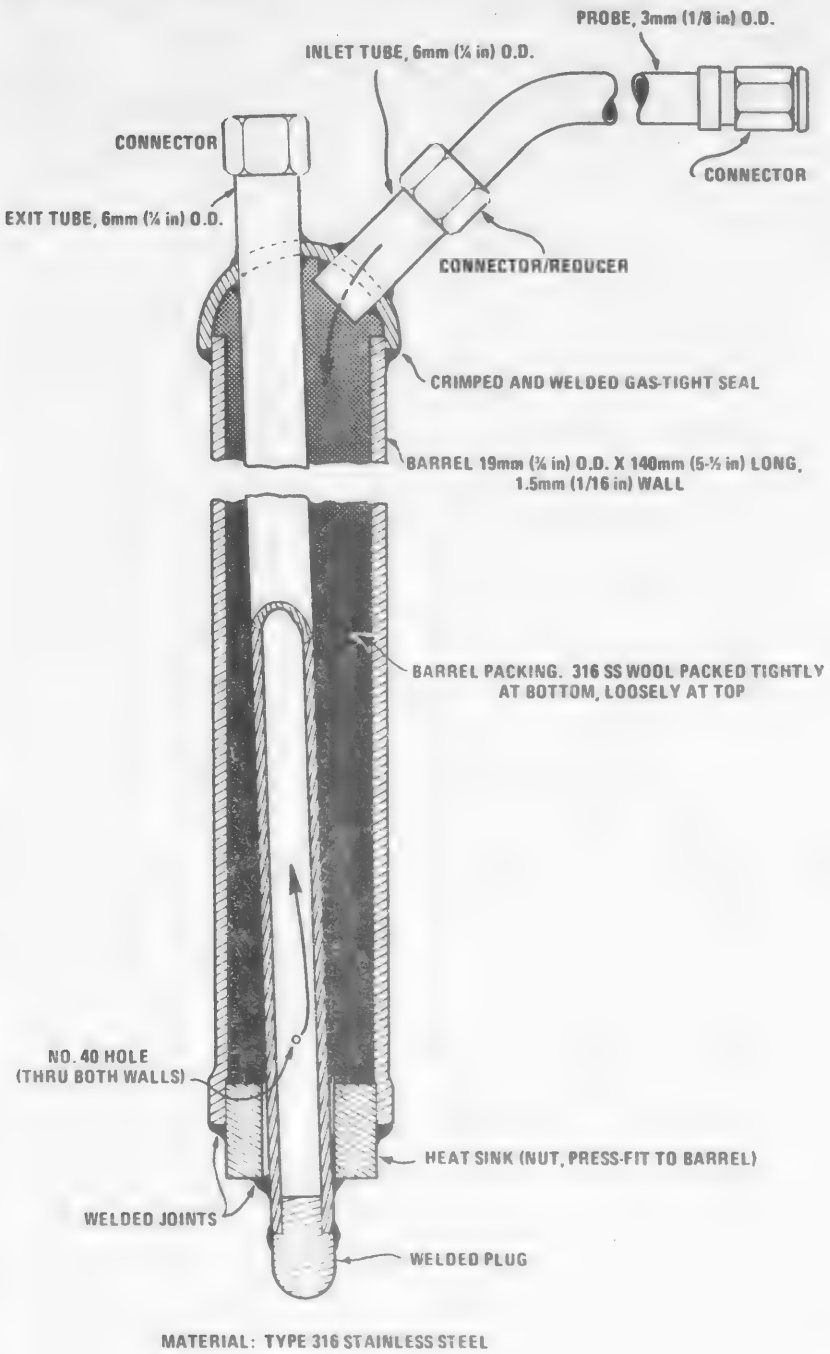
PROBE, 3mm (1/8 in) O.D.
INLET TUBE, 6mm (¼ in) O.D.
CONNECTOR
CONNECTOR
EXIT TUBE, 6mm (¼ in) O.D.
CONNECTOR/REDUCER
CRIMPED AND WELDED GAS-TIGHT SEAL
BARREL 19mm (¾ in) O.D. X 140mm (5-½ in) LONG, 1.5mm (1/16 in) WALL
BARREL PACKING. 316 SS WOOL PACKED TIGHTLY AT BOTTOM, LOOSELY AT TOP
NO. 40 HOLE (THRU BOTH WALLS)
HEAT SINK (NUT, PRESS-FIT TO BARREL)
WELDED JOINTS
WELDED PLUG
MATERIAL: TYPE 316 STAINLESS STEEL

Figure 5. Condensate trap[2].

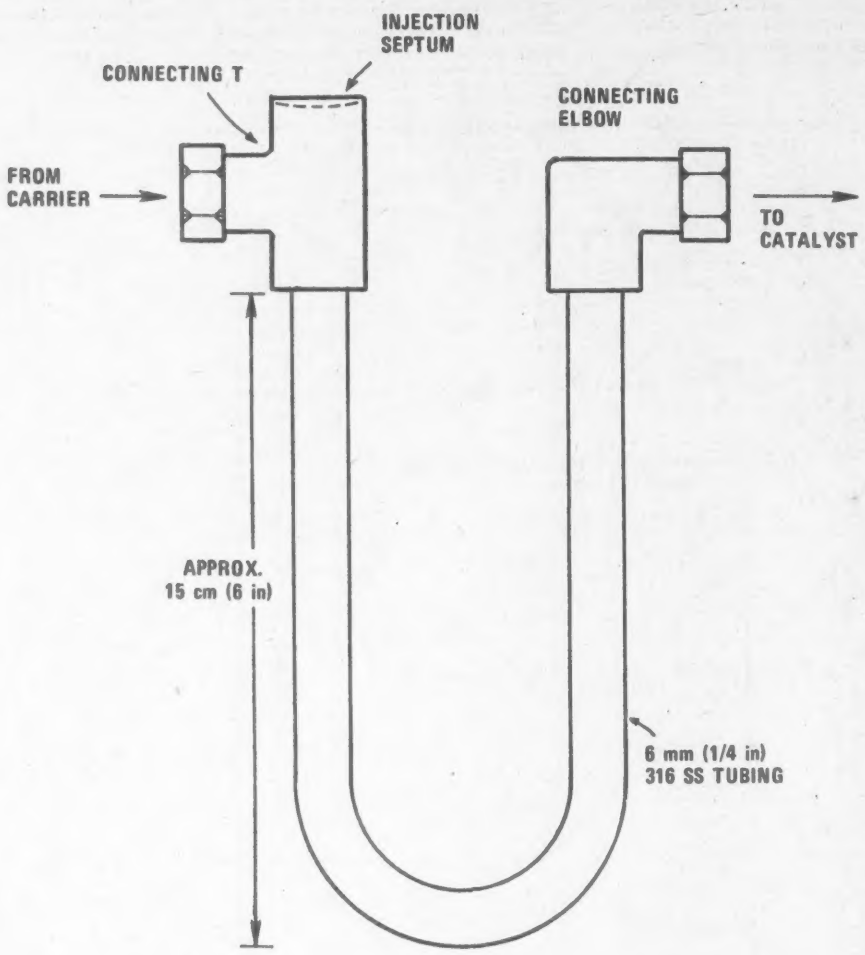

Figure 6. Liquid sample injection unit.

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

	TANK VACUUM, mm Hg / cm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)	(GAUGE)		
POST TEST (MANOMETER)	(GAUGE)		

LEAK RATE cm Hg / 10 min

PRETEST _____

POST TEST _____

TIME CLOCK/SAMPLE	GAUGE VACUUM, cm Hg	FLOWMETER SETTING	COMMENTS

Figure 7. Example Field Data Form.

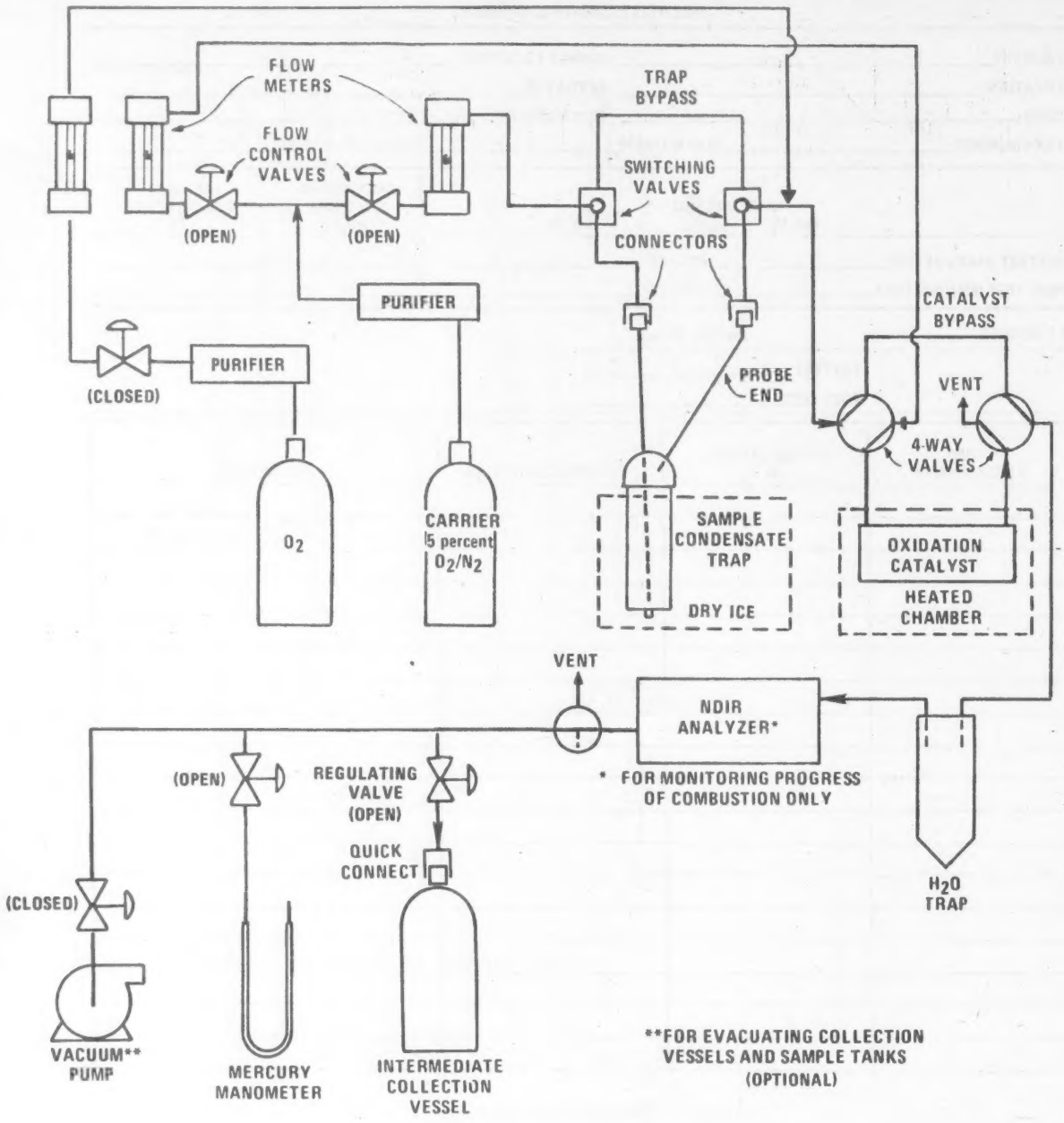

Figure 8. Condensate recovery and conditioning apparatus, carbon dioxide purge.

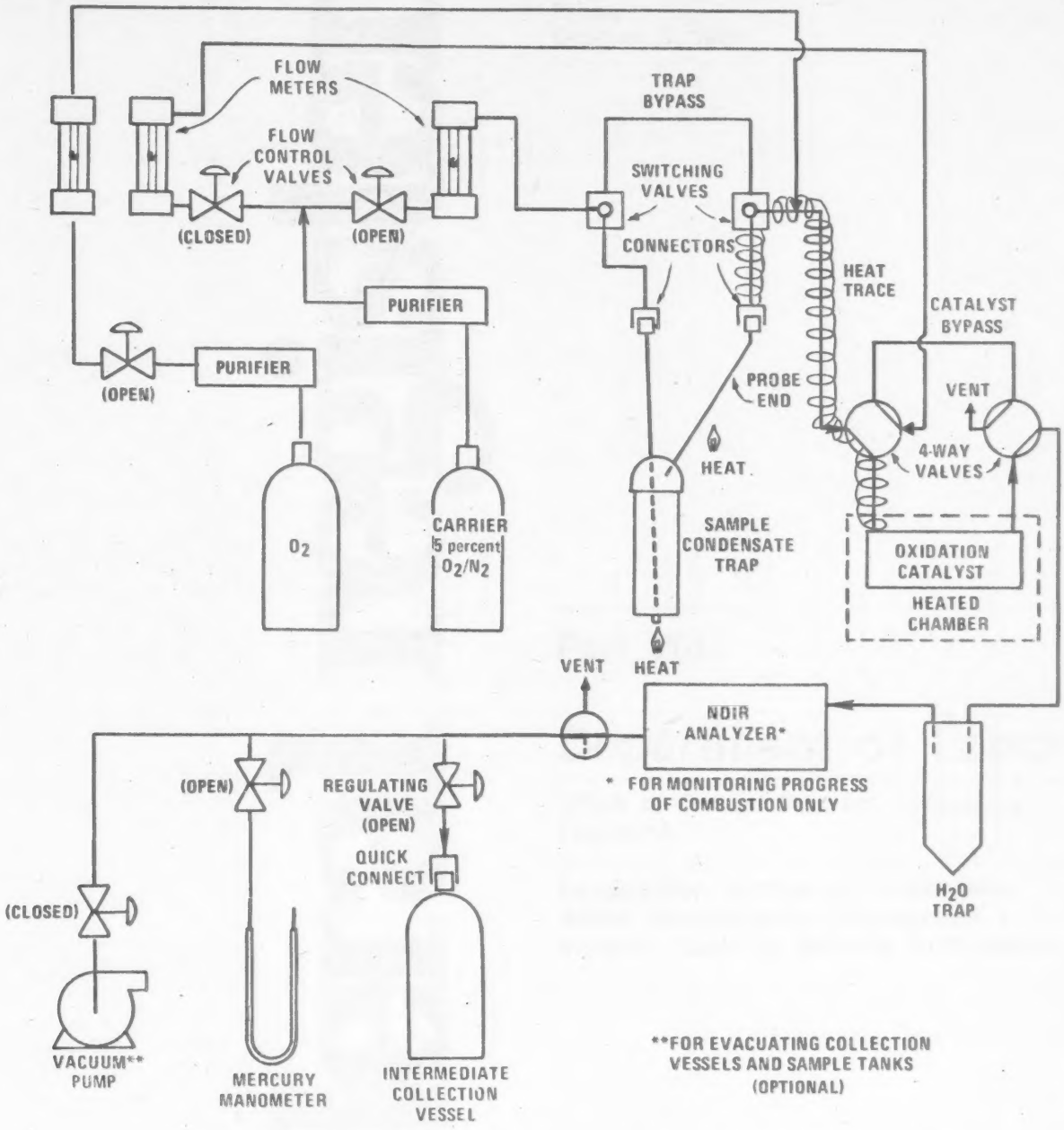

Figure 9. Condensate recovery and conditioning apparatus, collection of trap organics.

[FR Doc. 80-30716 Filed 10-2-80; 8:45 am]
BILLING CODE 6560-01-C